

SUMMARY

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‘STUDIES IN LIQUID CRYSTALLINE MATERIALS’

Liquid crystalline materials are being exploited for their different applications. New developments have further encouraged chemists to explore structural variations in the liquid crystalline materials in search of new liquid crystals for evaluating effect of chemical constitution on liquid crystalline properties and provide new materials for application oriented studies.

In the present study it was proposed to synthesize low molecular weight materials, monomers and polymers with special structural features.

Following mesogenic homologous series and the systems are synthesized and their mesogenic properties are studied..

- 1) Chiral and Achiral amido-esters
 - i) 4(4'-n-alkoxy benzoyloxy benzoyl)-4''-n-butoxy anilines (Series:I)
 - ii) 4(4'-n-alkoxy benzoyloxy benzoyl) 4''-S(+)-2-methyl butoxy anilines
(Series II)
- 2) Cholesteryl derivatives:
 - iii) Cholesteryl 4-(4'-n-alkoxy benzoyl)-amino benzoates (Series:III)
- 3) Other mesogenic compounds:
 - i) Biphenyl diesters:
 - ii) Cholesteryl 4-n-alkoxy benzoyl glycine (for C₄ and C₅ alkyl groups):
- 4) Side-chain mesogenic polymers:
 - i) Side-chain polymethacrylates with amide linkage.

- ii) Polymethacrylates with pendant cholesteryl moiety having flexible alkylene-carbonate spacers:
 - 5) Main-chain mesogenic polymers:
 - i) Polychalcones:
 - ii) Polyesteramides with azo central linkage and flexible spacer:
 - 6) Model compounds:
 - 7) Evaluation of different mesogenic compounds :
 - i) Molecular weight determination.
 - ii) X-ray diffraction analysis
 - iii) Conductivity study
 - iv) Fluorescent spectra
 - v) Thermo gravimetric analysis.
 - 8) Textures of different phases and characteristics of different phases by photomicrography
- (1) Chiral and Achiral amido-esters:**
- (i) 4(4'-n-alkoxy benzyloxy benzoyl)-4''-n-butoxy anilines (Series:I):
- Thirteen compounds have been synthesized and their mesogenic properties were evaluated. The methyl to n-propyl derivatives exhibit nematic mesophases. n-Butyl to n-decyl derivatives exhibit smectic and nematic mesophases. n-Dodecyl to n-octadecyl derivatives exhibit only smectic phases. All the smectic homologues exhibit smectic C phases. Middle members exhibit polymorphism of smectic mesophase. The plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits odd-even effect for nematic - isotropic transition temperatures.

(ii) 4(4'-n-alkoxy benzoyloxy benzoyl)-4''-S(+) 2-methyl butoxy anilines (Series **II**):

Ten compounds of the series were synthesized. In this series n-propyl to n-dodecyl derivatives exhibit smectic *C and cholesteric mesophases. n-Tetradecyl and n-hexadecyl derivatives exhibit only smectic *C phases. The plot of transition temperatures versus number of carbon atoms in alkoxy chain exhibits odd-even effect for cholesteric-isotropic transition temperatures. Two compounds were analysed by calorimetric study (C_{12} and C_{14}) to confirm the transition temperatures of the compounds which were observed under polarized microscope.

Eventhough there is a little difference in terminal alkoxy substituents between series I and II, due to chirality, series II exhibits cholesteric mesophase. The α -methyl group of chiral 2-methyl-butoxy substituent does not adversely affect the smectic properties of series II.

Reversal of amide linkage in series I and II compared to other similar systems has indicated that reversal enhances mesogenic properties of series I and II.

(2) Cholesteryl derivatives:

(iii) Cholesteryl 4-(4'-n-alkoxy benzoyl)-amino benzoates (series III)

Series III, though possesses amide linkage, it differs from series I and II, because it possesses cholesteryl moiety. The cholesterol imparts chirality, hence series III is also chiral.

Thirteen homologues were synthesized by condensing 4-(4'-n-alkoxy benzoyl)-amino benzoyl chlorides with cholesterol. Methyl to n-hexyl derivatives exhibit only cholesteric mesophases. n-Heptyl to n-dodecyl derivatives exhibit Sc and cholesteric phases. n-Tetradecyl to n-octadecyl derivatives exhibit Sc, S_A and

cholesteric phases. The plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibit odd-even effect and falling tendency for cholesteric-isotropic transition temperatures. The curve for the even members lies over the odd members. The Sc-cholesteric transition temperature curve rises to the maximum and then falls off. S_A to cholesteric transition temperature curve rises but does not merge with the falling cholesteric-isotropic transition temperature curve even in the n-octadecyl member.

All the compounds were characterized by elemental analysis and number of homologues of the three series were characterized by IR spectra and NMR spectra. All the three series exhibit polymorphism of the smectic phase.

The liquid crystalline behaviour of series III has further supported the view that amide central linkage enhances liquid crystalline properties of the system and enhancement is more in smectic phase thermal stabilities compared to schiff bases with similar structural features. Compounds exhibit cholesteric phases at very high temperatures and can be good candidates for high temperature thermography.

(3) Other Mesogenic Compounds:

(i) Biphenyl esters with flexible and rigid spacers (Siamistwins)

To understand behaviour of polymers, a few mesogenic compounds were synthesized by condensing aliphatic and aromatic dicarboxylic acid chlorides with 4-hydroxy-4'-nitrobiphenyl. Diester with four flexible methylene groups and one with p-phenylene unit exhibit nematic mesophase. However one would have expected second compound with two biphenylene and one p-phenylene unit in the molecule, to exhibit smectic mesophase. It seems presence of $-NO_2$ group on both the terminus, has strong effect on the induction of smectic mesophase.

(ii) Cholesteryl 4-n-alkoxy benzoyl glycines :

Cholesteryl derivatives of 4-n-butoxy and 4-n-pentyloxy benzoyl glycines were synthesized and characterized. Both the compound exhibit cholesteric phase of broad range and high transition temperatures. Cholesterol moiety with a flexible chain having amide linkage exhibits higher cholesteric thermal stability. These compounds can be used with other cholesterics for high temperature detection.

(4) Side chain mesogenic polymers:

Side chain liquid crystalline polymers are used in electronic storage devices.

(i) Side chain polymethacrylates with amide linkage.

Six monomeric methacrylates were synthesized by condensing different hydroxy alkyl methacrylates with 4-(4'-n-alkoxy benzoyl)-amino benzoyl chlorides. These monomers were polymerized by using solution polymerization technique. None of the monomers exhibit mesophases. All the polymethacrylates [with $(\text{CH}_2)_2$ and $(\text{CH}_2)_6$ flexible spacers], exhibit strong birefringence on cooling the melt with the shear force. However, polymer P₄ exhibits birefringence on heating as well as on cooling. It seems the melt results in homeotropic arrangement hence classical texture of nematic or smectic phase is not observed. The study indicates that side chain polymethacrylates having ester and amide linkages have high tendency to give homeotropic phases.

(ii) Polymethacrylates with pendant cholesteryl moiety having flexible alkylene-carbonate spacers:

Two monomers were synthesized by condensing hydroxy alkylene methacrylates with cholesteryl chloroformate having two and six methylene spacers.

Both the monomers are monotropic cholesteric. Both the monomers on polymerization gave oligomeric polymethacrylates.

Both the oligomers exhibit the texture similar to smectic C phases. Oligomers exhibit smectic *C phase on cooling upto room temperature indicating high supercooling tendency.

The copolymer of methacrylate of cholesteryl hydroxy ethyl carbonate with n-butylmethacrylate (80:20) exhibited enantiotropic smectic phase having texture like Sm *C phase.

(5) Main Chain mesogenic polymers

(i) Polychalcones:

Acid chlorides of 4,4'-dicarboxy- α , ω -diphenoxy alkanes $[(CH_2)_6, (CH_2)_{10}$ flexible spacers] were condensed with 4-amino-4'-hydroxy chalcone and 4,4'-dihydroxy chalcone. Solution condensation polymerization was carried out by condensing acid chlorides of 4,4'-dicarboxy , α , ω -diphenoxy alkanes $[(CH_2)_6, (CH_2)_{10}$ flexible spacers] with 4-amino-4'-hydroxy chalcone and 4,4'-dihydroxy chalcone. All the polymers (EP-1 to EP-4) exhibit nematic mesophases. The transition temperatures are lower compared to similar polymers with shorter flexible spacers. All the polymers exhibit fluorescence behaviour

(ii) Polyesteramides with azo central linkage and flexible spacer:

In continuation of our earlier study three polymers are synthesized by condensing acid chlorides of 4,4'-dicarboxy-1,6-diphenoxy hexane with substituted 4-hydroxy-4'-amino azobenzenes. All the three polymers exhibit nematic phases of high thermal stability.

(6) Model Compounds:

Model compounds help to understand mesogenic properties of polymers with this in view model compounds are synthesized having combination of an ester and an amide linkage followed with flexible or rigid core.

Compounds AE-1 to AE-4 were obtained by condensing 4-n-alkoxy benzoyloxy benzoyl chloride (C_4 and C_8) with p-amino phenol and monoethanol amine, respectively.

All the four model compounds having an ester and an amide linkage exhibit nematic mesophase. Compounds with flexible spacer exhibit lower temperature mesophases. In the case of aliphatic spacers the length of alkoxy chain has strong effect on the incidence of the smectic phase.

In the case of model compounds where diamide central linkage is introduced, having structural similarity with above compounds do not exhibit mesomorphism (AE-5 and AE-6 compounds).

Three model compounds with flexible diester linkage and substituted azo phenyl linkage exhibit nematic mesophase.

The study of the model compounds indicated that even slight variation in central linkage and/or the terminal alkoxy chains have marked effect on the incidence of mesophase as well as on the type of the mesophase.

All the compounds were characterized by elemental analysis. Number of compounds were evaluated by IR, NMR and DSC spectra. All polymers were further evaluated by using viscosity.

(7) Evaluation of different mesogenic compounds:**(i) Molecular weight determination:**

Molecular weight of four polymeric samples was determined by using GPC technique. Polystyrene was used as standard. The samples have low molecular weight that indicates they are oligomeric mesogens.

(ii) X-ray diffraction analysis

Four polymer samples were studied by X-ray diffraction analysis. Two polymers (P_7 & P_8) show slight crystallinity but largely the polymers are amorphous, one polymer (P_1) shows amorphous and one polymer (P_2) shows weak and strong peaks indicating crystalline in nature.

(iii) Conductivity study:

Four polymer samples were studied by a four probe technique by measuring resistivity at various temperatures, i.e. from room temperature upto the temperature which is less than transition temperatures of polymers. At lower temperature, the conductivity decreases with increase in temperature and on cooling conductivity increases with decrease in temperature. Polymers exhibit semiconducting tendencies.

(iv) Fluorescent spectra:

Seven monomers, nine polymers and one co-polymer were studied. The fluorescent spectra of monomers are quite comparable with polymers. The monomers, polymers and co-polymer show good fluorescent properties.

(v) Thermogravimetric analysis:

Thirteen polymers were analysed and they exhibit good thermal stability. Most of the polymers were quite stable upto 250°-300°C.